Mechanism of the direct hydrodenitrogenation of naphthylamine on sulfided $NiMo/Al_2O_3$

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The hydrodenitrogenation of 1-naphthylamine was studied over a sulfided $NiMo/Al_2O_3$ catalyst between 300 and 350 °C. 1-Naphthylamine reacted to tetralin, naphthalene, 1,2-dihydronaphthalene and 5,6,7,8-tetrahydro-1-naphthylamine. To elucidate the reaction mechanism, the reactions of the intermediates 1,2,3,4-tetrahydro-1-naphthylamine, 1,2-dihydronaphthalene and 5,6,7,8-tetrahydro-1-naphthylamine were studied as well. The results show that 1-naphthylamine reacts through hydrogenation to 1,2,3,4-tetrahydro-1-naphthylamine, which reacts by NH_3 elimination to 1,2-dihydronaphthalene. The latter molecule subsequently reacts by hydrogenation to tetralin as well as by dehydrogenation to naphthalene. In addition, naphthalene is formed by direct denitrogenation from 1-naphthylamine. This direct denitrogenation may take place by hydrogenation of 1-naphthylamine to 1,2-dihydro-1-naphthylamine, followed by NH_3 elimination or followed by a Bucherer-type NH_2–SH exchange, dehydrogenation and C–S bond hydrogenolysis.

KEY WORDS: naphthylamine; hydrodenitrogenation; hydrogenolysis; direct denitrogenation; direct desulfurization; hydrotreating catalysts.

1. Introduction

The cleavage of a carbon–nitrogen (C–N) or a carbon–sulfur (C–S) bond is a crucial step in hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions respectively. Hydrogenation of the aromatic ring that contains the S atom does not seem to be required for the removal of the S atom, because thiophenol reacts almost exclusively to benzene under HDS conditions [1], while about 80% of dibenzothiophene reacts to biphenyl [2]. This suggests that the relatively weak C–S bond can be broken by hydrogenolysis. Hydrogenolysis is used here in the mechanistic sense, meaning a reaction on the catalyst surface in which a C–X bond is broken and C–H and H–X bonds are formed before the product molecule leaves the catalyst surface. Homolytic C–S bond breaking (hydrogenolysis) was demonstrated in the homogeneous reaction of aliphatic and aryl thiols on sulfur-containing Mo–Co clusters [3]. Breaking of the C–S bond might occur by nucleophilic aromatic substitution by a hydride ion as well [4]. It has also been suggested, however, that the hydrogenolysis of the C–S bond (also called direct desulfurization) is only apparent and actually occurs by hydrogenation of a neighboring C–C bond, followed by H_2S elimination [2,5].

The main reactions involved in the removal of an N atom from aromatic compounds are hydrogenation of the aromatic ring that contains the nitrogen atom, and breaking of the resulting aliphatic C–N bonds to a hydrocarbon molecule and ammonia [1,6–9]. Aliphatic C–N bond breaking occurs either by elimination [6,7], or by nucleophilic substitution by H_2S followed by C–S bond hydrogenolysis [6,8]. The main HDN product of aniline is therefore cyclohexane, which is formed via cyclohexylamine and cyclohexene [1,8]. Similarly, the main product in the HDN of quinoline is propylcyclohexane [9].

Direct breaking of the C–N bond in aniline (also called direct denitrogenation) occurs to a minor degree as well. For instance, in the HDN of *o*-propylaniline the selectivity to propylbenzene was 7% over a $NiMo/Al_2O_3$ catalyst and 24% over a Mo/Al_2O_3 catalyst [10]. For fused aromatic amines such as naphthylamine (NA) and anthracylamine, direct C–N bond breakage is even more important [11]. If this direct C–N bond breakage in an arylamine occurs by real hydrogenolysis in the mechanistic sense, then one should expect that hydrogenolysis of an alkylamine is even easier. The reason for this is that the C–N bond in alkylamines is weaker than the C–N bond in arylamines because of the conjugation of the NH_2 group with the aromatic ring. Nevertheless, alkylamines seem to react exclusively by β-hydrogen elimination and nucleophilic substitution by H_2S followed by C–S bond hydrogenolysis [6–9]. This suggests that hydrogenolysis in arylamines may not be real but apparent, meaning that the reaction occurs via an indirect, multi-step mechanism.

To determine whether the hydrogenolysis of an aryl C–N bond is real or apparent, we studied the HDN of

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1-naphthylamine and the reactions of the possible intermediates 1,2,3,4-tetrahydro-1-naphthylamine, 1,2-dihydronaphthalene and 5,6,7,8-tetrahydro-1-naphthylamine.

2. Experimental

2.1. Materials and sample preparation

The $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts were prepared by co-impregnation of $\gamma-Al_2O_3$ (*Condea*, BET surface area 210 m^2 g^{-1}, total pore volume 0.44 cm^3 g^{-1}, particle size 90–125 μm) with aqueous solutions of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$ and nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ or cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ (all from Fluka, purum p.a.) in amounts necessary to obtain a loading of 3 wt% Ni or Co and 8 wt% Mo. Prior to impregnation, the alumina support was dried overnight at 120 °C. After impregnation, the material was again dried overnight in air at 120 °C.

For the purpose of solubility, 1-naphthylamine (Aldrich, 98%), 1,2,3,4-tetrahydro-1-naphthylamine (Acros, 98%), 1,2-dihydronaphthalene (Fluka, 98%), 5,6,7,8-tetrahydro-1-naphthylamine (Aldrich, 99%), tetralin (ABCR) and naphthalene (ABCR) were dissolved in benzene or toluene (Fluka, puriss. p.a.). The gases used were hydrogen (PanGas 4.0), a mixture of 10% H_2S in H_2 (Messer Griesheim 3.0) and nitrogen (PanGas 4.5).

2.2. Sulfidation and reaction

The catalytic experiments were performed in a stirred 17-ml autoclave as well as in a microflow reactor. The $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts that were used in the autoclave were sulfided in a glass-flow reactor by heating at 5 °C min^{-1} and then sulfiding at 400 °C for 4 h in a mixture of 10% H_2S in H_2. Thereafter, nitrogen was passed through the reactor at the same temperature for 0.5 h and subsequently the catalysts were cooled to room temperature. The reactor was opened to air at room temperature. An amount of 5 to 10 mg of catalyst was transferred to the autoclave and resulfided for 1 h in a mixture of 10% H_2S in H_2 at 400 °C (heating rate 5 °C min^{-1}) and 0.35 MPa. After resulfidation, the catalyst was cooled to room temperature, the autoclave was opened and the reaction mixture (0.6 or 1.0 ml) was added quickly. After closing the autoclave, hydrogen was added up to 0.6 MPa at room temperature and the temperature was increased to the reaction temperature (between 300 and 350 °C). Liquid samples of 0.05 to 0.1 ml were collected at different times and analyzed off-line by gas chromatography (Shimadzu GC-14 B), using an HP1 (cross-linked methyl siloxane) or a DB-5ms (5%-phenyl methylpolysiloxane) column and a flame ionization detector.

The experiments in the microflow reactor were carried out with the $NiMo/Al_2O_3$ catalyst only. A sample of 0.02 g $NiMo/Al_2O_3$ diluted with 8 g SiC was first dried for 2 h at 400 °C and then sulfided for 4 h *in situ* with a mixture of 10% H_2S in H_2 at 1 MPa. After sulfidation, the pressure was increased to reaction pressure and the solution of the reactant in toluene was fed to the reactor with a high-pressure syringe pump. For further experimental details see [12].

3. Results

Both catalysts were active in the HDN of 1-naphthylamine in the autoclave and the conversion after 1 h at 300 °C was 22% over $NiMo/Al_2O_3$ and 33% over $CoMo/Al_2O_3$. 1-Naphthylamine reacted to tetrahydronaphthalene (tetralin), 1,2-dihydronaphthalene, naphthalene and a small amount of 5,6,7,8-tetrahydro-1-naphthylamine. The selectivity to 1,2-dihydronaphthalene decreased with reaction time and no 1,2-dihydronaphthalene was observed after 30 min over $CoMo/Al_2O_3$, while over $NiMo/Al_2O_3$ the selectivity to 1,2-dihydronaphthalene decreased more slowly (figure 1). At short reaction time, the selectivities to naphthalene and 1,2-dihydronaphthalene were high and increased with decreasing reaction time, while the reverse was true for tetralin (figure 2). This indicates that naphthalene and 1,2-dihydronaphthalene are formed earlier and tetralin later in the reaction network. At the higher temperature of 350 °C, the conversion was 70% after 1 h and more naphthalene and less tetralin were formed than at 300 °C. 1,2-Dihydronaphthalene was only produced at short reaction time.

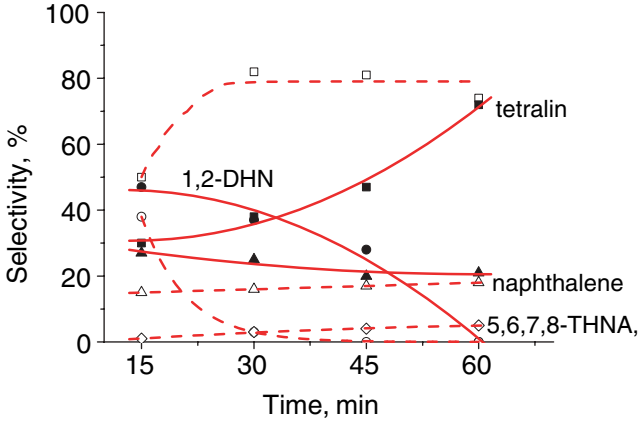


Figure 1. Selectivities in the HDN of 1-naphthylamine over $NiMo/Al_2O_3$ (closed symbols) and $CoMo/Al_2O_3$ (open symbols) catalysts at 300 °C and 0.6 MPa in the autoclave1 (1,2-DHA = 1,2-dihydronaphthalene}, 5,6,7,8-THNA = 5,6,7,8-tetrahydro-1-naphthylamine).

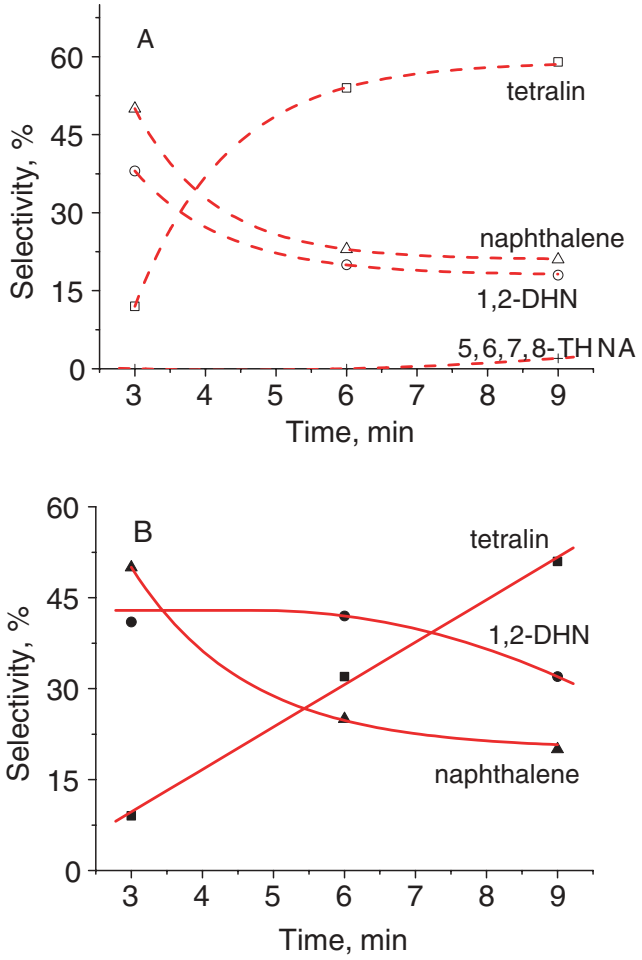


Figure 2. Selectivities in the HDN of 1-naphthylamine over (A) $CoMo/Al_2O_3$ and (B) $NiMo/Al_2O_3$ catalysts at 300 °C and 0.6 MPa at short reaction times in the autoclave (1, 2-DHN = 1, 2-dihydronaphthalene, 5, 6, 7, 8-THNA = 5, 6, 7, 8-tetrahydro-1-naphthylamine).

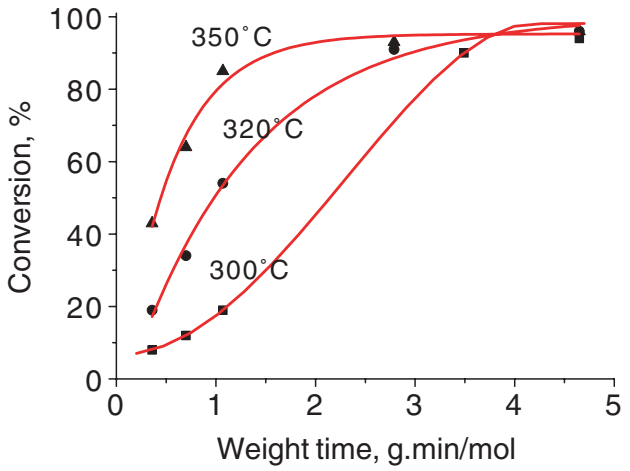


Figure 3. Conversion of 1-naphthylamine over $NiMo/Al_2O_3$ in the microflow reactor at 3 MPa, 10 kPa H_2S and 300, 320 and 350 °C.

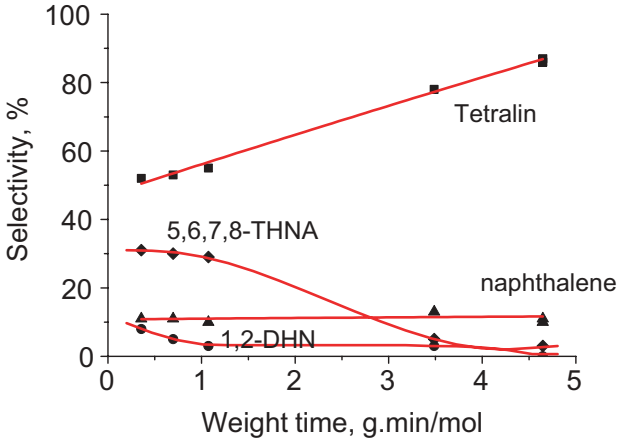


Figure 4. Product selectivities in the HDN of 1-naphthylamine over $NiMo/Al_2O_3$ at 300 °C, 3 MPa and 10 kPa H_2S in the microflow reactor (1, 2-DHN = 1, 2-dihydronaphthalene, 5,6,7,8-THNA = 5,6,7,8-tetrahydro-1-naphthylamine).

The conversions in the experiments in the microflow reactor over $NiMo/Al_2O_3$ were always much higher than that in the autoclave, the main reason being the five-times higher H_2 pressure. Conversions and product selectivities are presented in figures 3 and 4 respectively. At 300 °C and 3 MPa, in the presence of 10 kPa H_2S, tetralin, 5,6,7,8-tetrahydro-1-naphthylamine, naphthalene and 1,2-dihydronaphthalene behaved like primary products with non-zero selectivities at zero weight time. The selectivity to 1,2-dihydronaphthalene was very sensitive to the temperature and H_2 pressure. It decreased with increasing H_2 pressure and increasing temperature (table 1). At low weight time, the selectivity to 5,6,7,8-tetrahydro-1-naphthylamine was 30%, but it decreased to zero at high conversion (figure 4). The naphthalene selectivity was constant at about 10%. Since the tetralin selectivity increased with weight time, the naphthalene to tetralin ratio decreased with weight time (figure 5). This ratio was more sensitive to temperature than to H_2 pressure (table 1).

Table 1
Selectivity to 1,2-dihydronaphthalene (DHN) in the reaction of 1-naphthylamine (NA), and the naphthalene to tetralin ratio (N/T) in the reactions of NA, 1,2,3,4-tetrahydro-1-naphthylamine (THAN) and DHN at 10 kPa H_2S and $\tau = 1.07$ g min mol^{-1}

Conditions		% DHN	N/T		
T (°C)	P (MPa)	NA	NA	THAN	DHN
300	1	13	0.22		
300	2	6	0.20		
300	3	3	0.20	0.10	0.10
320	3	0	0.26		
350	3	0	0.37	0.19	0.22

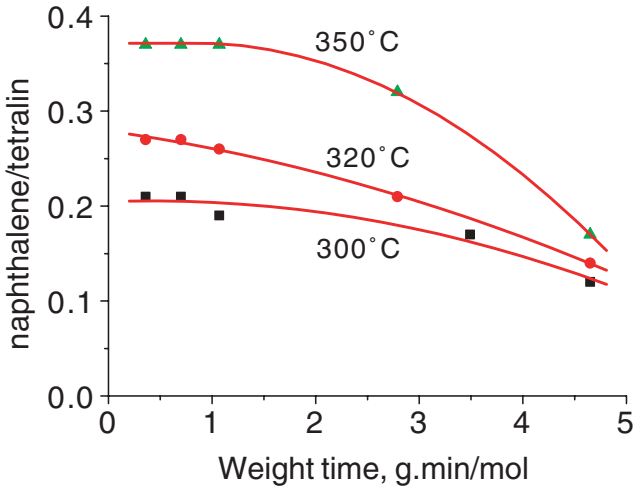


Figure 5. Naphthalene to tetralin ratio in the HDN of 1-naphthylamine over $NiMo/Al_2O_3$ at 3 MPa, 10 kPa H_2S and 300, 320 and 350 °C.

To compare the reaction rates of potential intermediates in the HDN of 1-naphthylamine, we also measured the HDN of 1,2,3,4-tetrahydro-1-naphthylamine and 5,6,7,8-tetrahydro-1-naphthylamine and the hydrogenation of 1,2-dihydronaphthalene, the latter in the presence of aniline to simulate the inhibiting effect of an arylamine. At 300 °C, 3 MPa and 10 kPa H_2S, the conversions of 1,2,3,4-tetrahydro-1-naphthylamine and 1,2-dihydronaphthalene were already complete at the lowest weight time possible in our microflow reactor ($\tau = 1.07$ g.min mol^{-1}). These conversions of 100% were much higher than that of 1-naphthylamine (20%). The only products were tetralin and naphthalene. Figure 6 shows the naphthalene to tetralin ratio as a function of time for 1,2,3,4-tetrahydro-1-naphthylamine at 300 and 350 °C and at 10 kPa H_2S; almost identical curves were obtained for 1,2-dihydronaphthalene. Because of the complete conversion of 1,2,3,4-tetrahydro-1-naphthylamine and 1,2-dihydronaphthalene already at short weight time, the naphthalene to tetralin ratios decreased with time because of the hydrogenation of naphthalene to tetralin and the fact that initially a larger amount of naphthalene was produced than corresponding with thermodynamics. The naphthalene to tetralin ratios, extrapolated to $\tau = 0$ g.min mol^{-1} for the reactions of 1,2,3,4-tetrahydro-1-naphthylamine and 1,2-dihydronaphthalene, were 0.24 and 0.27 respectively at 350 °C and 3 MPa, and the ratio was 0.11 for both reactions at 300 °C and 3 MPa. These values are much lower than the values of 0.37 (350 °C, 3 MPa) and 0.21 (300 °C, 3 MPa) obtained in the HDN of 1-naphthylamine itself (figure 5).

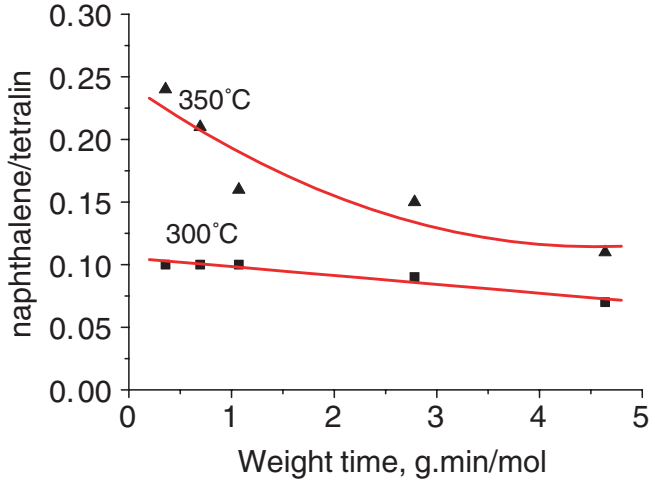


Figure 6. Naphthalene to tetralin ratio in the HDN of 1,2,3,4-tetrahydro-1-naphthylamine over $NiMo/Al_2O_3$ at 3 MPa, 10 kPa H_2S and 300 and 350 °C.

The conversion of 5,6,7,8-tetrahydro-1-naphthylamine at 300 °C, 3 MPa and 10 kPa H_2S was only 3% at $\tau = 1.07$ g.min mol^{-1}. This indicates that its low selectivity in the HDN of 1-naphthylamine is not due to a fast subsequent reaction, but to a relatively slow rate of formation.

4. Discussion

4.1. Direct denitrogenation

Our results confirm that hydrogenolysis of arylamine C–N bonds is possible, since naphthalene behaved like a primary product on sulfided $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts. The other main products of the reaction were 1,2-dihydronaphthalene, tetralin and 5,6,7,8-tetrahydronaphthylamine; they result from hydrogenation. The ratio of hydrogenolysis to hydrogenation strongly depended on the reaction temperature: the higher the reaction temperature, the higher the ratio. Similar behavior was observed in the HDN of aniline over a sulfided NiW/Al_2O_3 catalyst [13].

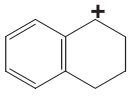
The experiments at lower pressure in the autoclave as well as in the microflow reactor demonstrated that both naphthalene and 1,2-dihydronaphthalene behave as primary products, with selectivities increasing at shorter reaction time. Whereas naphthalene can be envisaged to be formed directly from 1-naphthylamine (*e.g.*, by hydrogenolysis), the formation of 1,2-dihydronaphthalene from 1-naphthylamine has to occur through at least one intermediate. A logic intermediate would be 1,2,3,4-tetrahydro-1-naphthylamine. This intermediate is very reactive under our conditions, as shown in the separate experiment in which 1,2,3,4-tetrahydro-1-naphthylamine already completely reacted to tetraline and naphthalene at the lowest weight time possible in our microflow reactor. 1,2-Dihydronaphthalene, the expected primary product obtained by NH_3 elimination of 1,2,3,4-tetrahydro-1-naphthylamine, was not observed in this experiment, as it reacts very fast as well. The very high reactivity of 1,2,3,4-tetrahydro-1-naphthylamine also explains why it was not observed in the HDN of 1-naphthylamine even after a short reaction time. This is

in accordance with results obtained in the HDN of *o*-methylaniline, for which the first hydrogenation step was also much slower than the subsequent nitrogen-removal step [14]. In that reaction, the hydrogenated intermediate *o*-methylcyclohexylamine was only observed when a large amount of cyclohexene was added during reaction, to cause the intermediate to leave the catalyst surface. When an arylamine is hydrogenated at the catalyst surface, the intermediate cyclohexylamine apparently undergoes ammonia elimination faster than when it desorbs from the surface and diffuses out of the catalyst pores. Furthermore, in the case of 1,2,3,4-tetrahydro-1-naphthylamine, the denitrogenation might be even very fast because it can take place by an E_1 elimination mechanism. The reason is that the carbocation resulting from tetrahydronaphthalene (scheme 1) is strongly stabilized by conjugation with the aromatic ring and by electron donation from the βCH_2 group.

Because 1,2-dihydronaphthalene reacts fast but not extremely fast, it could be detected and seen to behave as a primary product. Higher temperature and H_2 pressure increase the rate of the reaction of 1,2-dihydronaphthalene. This explains why at 3 MPa and 300 or 350 °C, this intermediate was not observed. The microflow experiment showed that 1,2-dihydronaphthalene reacts to a 9 : 1 mixture of tetralin and naphthalene at short weight time. Apparently, hydrogenation as well as dehydrogenation can take place quickly.

The much higher naphthalene to tetralin ratios observed in the HDN of 1-naphthylamine than in the reaction of 1,2-dihydronaphthalene (figures 5 and 6 and table 1) indicate that 1,2-dihydronaphthalene is not the only source of naphthalene. The different behavior of naphthalene and tetralin as a function of reaction time confirms this (figure 2): naphthalene behaves as a primary product and tetralin as a secondary product. This means that additional naphthalene must be formed by a reaction that takes place earlier in the reaction network than the formation of 1,2-dihydronaphthalene from 1,2,3,4-tetrahydro-1-naphthylamine. 1,2-Dihydro-1-naphthylamine or 1-naphthylamine could be intermediates for the formation of this naphthalene.

Moreau *et al*. proposed that the naphthalene that forms in the HDN of 1-naphthylamine can be partially hydrogenated to tetralin [11]. To check this, we performed a hydrogenation of 1-methylnaphthalene in the presence of 1-naphthylamine over sulfided $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ at 300 °C in the autoclave, but we did not observe any products of the hydrogenation of 1-methylnaphthalene. This shows that the naphthalene-to-tetralin step does not take place during the HDN of 1-naphthylamine as long as the 1-naphthylamine concentration is high enough to inhibit the hydrogenation of aromatic molecules. This corroborates the results obtained in the reaction of ethylbenzene in the presence of *o*-propylaniline, in which ethylbenzene hydrogenation was only 1% over a $NiMo/Al_2O_3$ catalyst at 350 °C and at 60% conversion of *o*-propylaniline [12].

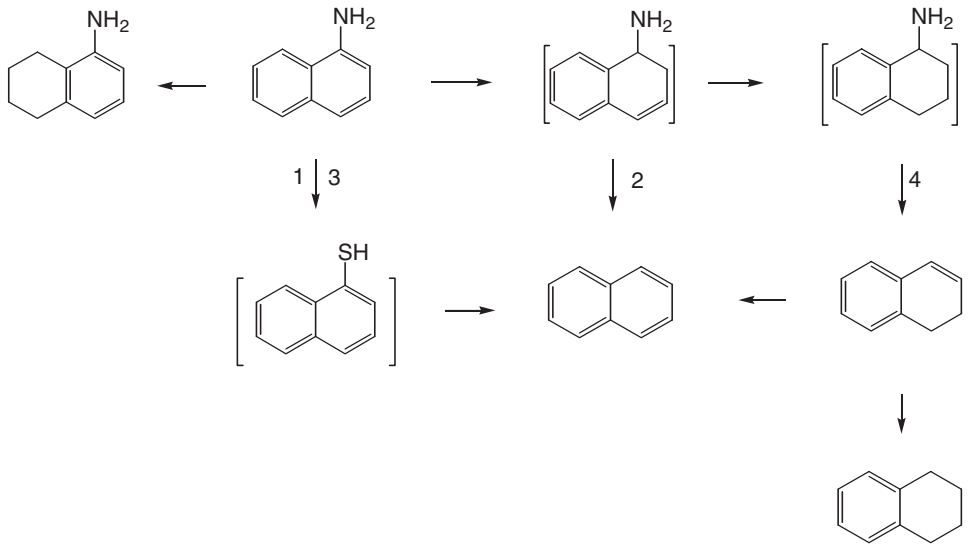


Scheme 1. Carbocation of tetrahydronaphthalene.

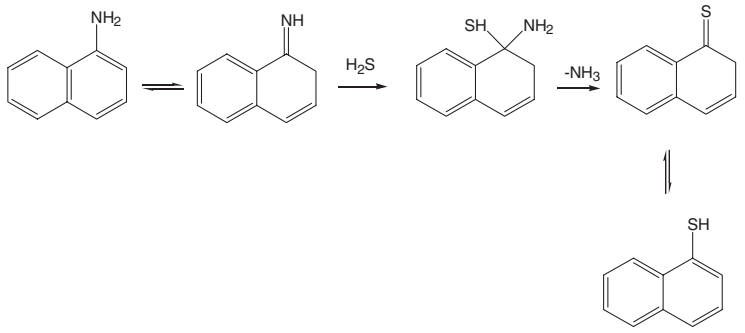
On the basis of our results, we propose a mechanism for the HDN of 1-naphthylamine over sulfided $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts (scheme 2) that differs in some points from that proposed by Moreau *et al*. [11]. There are two pathways, the main one being a multistep reaction pathway. First, 1-naphthylamine is partially hydrogenated to 1,2,3,4-tetrahydro-1-naphthylamine. This intermediate eliminates NH_3 and the resulting 1,2-dihydronaphthalene reacts to tetralin and naphthalene.

In the second pathway, 1-naphthylamine undergoes direct breaking of the C–N bond to naphthalene. The question is, if this reaction is really taking place, for instance, by homolytic splitting of the C–N bond and fast hydrogenation of the resulting radicals (like the C–S bond breaking in thiols [3]) or by the substitution of the amine group by a hydride ion [4]. It is also possible that the formed naphthalene gives the impression that 1-naphthylamine reacts by hydrogenolysis, but here, this is not the case. For instance, the transformation of 1-naphthylamine to 1-naphthylthiol by NH_2–SH exchange [9] and fast reaction of 1-naphthylthiol to naphthalene by hydrogenolysis of the C–S bond would look like C–N hydrogenolysis if 1-naphthylthiol were not observed (route 1 in scheme 2). The NH_2–SH exchange (scheme 3) would certainly be enhanced in arylamines with fused aromatic rings like naphthyl and anthracylamine, because the aromaticity of fused rings decreases with increasing number of rings. Thus, the 1,2-C–C bond in naphthalene has more double bond character than a C–C bond in benzene and the enamine character of 1-naphthylamine is stronger than that of aniline. The higher enamine contribution in turn means that the imine character is also higher because of the enamine–imine tautomeric equilibrium. This is analogous to the greater importance of the keto form in the enol–keto tautomeric equilibrium for naphthol than that for phenol [16]. As a result of the greater imine character, the addition of H_2S to 1-naphthylamine will be easier.

Also, the partial hydrogenation of 1-naphthylamine to 1,2-dihydro-1-naphthylamine followed by the fast elimination of NH_3 and the formation of naphthalene, would give the impression that hydrogenolysis had occurred (route 2 in scheme 2). The formation of a dihydro compound seems feasible and has already been proposed as an explanation for the apparent hydrogenolysis of dibenzothiophene [5]. At first sight, this explanation seems flawed because, owing to the planar



Scheme 2. Reaction mechanism for the HDN of 1-naphthylamine.



Scheme 3. Reaction from 1-naphthylamine to 1-thionaphthol by enamine–imine tautomerism, NH_2–SH exchange by addition of H_2S and elimination of NH_3, and thioenol–thioketo tautomerism.

structure of the cyclohexadiene molecule, the NH_2 group on the C1 atom and the H atom on the neighboring C2 atom are in the eclipsed conformation. This would mean that the subsequent elimination (e.g. of 1,2-dihydro-aniline to benzene and ammonia) must occur by *syn*-elimination although elimination tends to occur in the anti-periplanar rather than in the *syn*-antiplanar conformation [16]. A closer look at 1,2-dihydro-aniline suggests, however, that the elimination will not occur by an E2 mechanism, but by an E1 mechanism. The reason is that the carbon atom that bears the NH_2 group is in α position to the C3–C6 butadiene fragment. As a consequence, the cyclohexadienyl carbocation resulting from scission of the C–N bond will be strongly stabilized by conjugation with this butadiene fragment (scheme 4). An E1 elimination mechanism means, however, that the eclipsed conformation of the NH_2 group on the C1 atom and the H atom on the C atom in 1,2-dihydro-aniline is not an obstacle anymore against elimination.

Scheme 4. Cyclohexadienyl carbocation.

Another explanation for the direct denitrogenation would be to assume that aniline is hydrogenated to tetrahydroaniline, which undergoes elimination to cyclohexadiene. Cyclohexadiene then quickly reacts to cyclohexene or benzene. Since tetrahydroaniline is not flat, the elimination of ammonia is possible in the anticonformation. In our case of 1-naphthylamine, this means that the naphthalene would be formed via 1,2,3,4-tetrahydro-1-naphthylamine (route 4, scheme 2). This is, however, in contradiction to the naphthalene-to-tetralin ratio observed in the reaction of 1,2,3,4-tetrahydro-1-naphthylamine, which is two times lower than that observed in the reaction of 1-naphthylamine. Also, the ratio in the reaction of 1,2-dihydronaphthalene, the primary product of 1,2,3,4-tetrahydro-1-naphthylamine, is lower by a factor 2. We conclude that a tetrahydro intermediate cannot explain the direct denitrogenation of 1-naphthylamine to naphthalene.

1,2-Dihydro-1-naphthylamine may not only react to naphthalene by elimination of NH_3 but also by a

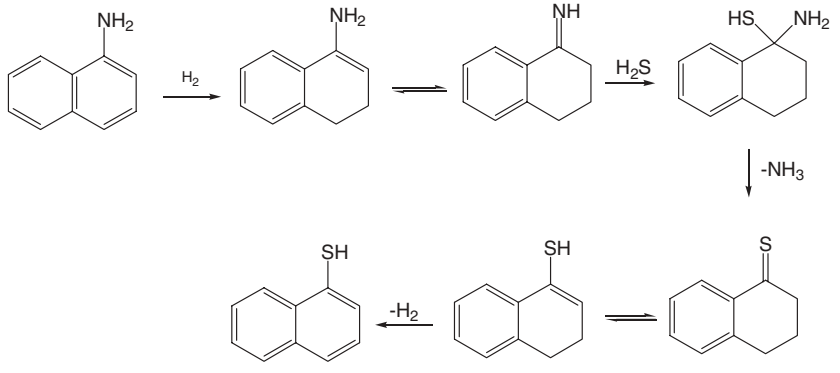
Bucherer-like NH_2–SH exchange of the amino group of 1,2-dihydro-1-naphthylamine by addition of NH_3 and elimination of H_2S via enamine–imine and thioenol–thioketo tautomeric equilibria (scheme 5 and route 3 in scheme 2). The resulting 1,2-dihydro-1-thionaphthol may dehydrogenate to 1-thionaphthol, which quickly undergoes hydrogenolysis to naphthalene. A dihydro intermediate could thus explain direct hydrogenation via a Bucherer-type NH_2–SH exchange reaction (scheme 4). Alternatively, NH_2–SH exchange could occur directly in the arylamine via the imine form of the enamine–imine tautomeric equilibrium (scheme 3).

Three mechanisms have thus been identified that can explain the apparent direct C–N bond breaking in 1-naphthylamine to naphthalene. In the first mechanism (scheme 3, route 1 in scheme 2), NH_2–SH exchange via the imine form of 1-naphthylamine is followed by hydrogenolysis of the C–S bond of 1-thionaphthol, while in the second mechanism the hydrogenation of 1-naphthylamine to 1,2-dihydro-1-naphthylamine is followed by NH_3 elimination (route 2 in scheme 2). A third mechanism would be that 1-naphthylamine is hydrogenated to a dihydro intermediate that undergoes a Bucherer-type NH_2–SH exchange reaction (scheme 5, route 3 in scheme 2). Some experimental observations speak in favor of the second and the third alternatives. It has been observed that the ratio of direct versus indirect C–N bond breaking depends on the catalyst, but is independent of a change in support and the addition of fluorine to the catalyst. Thus, a change from Al_2O_3 to silica–alumina and fluorination of these supports did not change the toluene to methylcyclohexane product ratio in the HDN of *o*-toluidine, although they did improve the activity [17]. This suggests that direct and indirect C–N bond breaking go through a common intermediate, which could be a dihydro intermediate. That would eliminate route 1 (scheme 2), but would still leave route 2 (scheme 2) (hydrogenation followed by NH_3 elimination) and route 3 (hydrogenation followed by a Bucherer-type NH_2–SH exchange, dehydrogenation and C–S hydrogenolysis) as possibilities to explain the direct C–N bond breaking. The ratio of direct to indirect C–N bond breaking would then be determined by the ratio of the two reactions that dihydro-1-naphthylamine can undergo: further hydrogenation to 1,2,3,4-tetrahydro-1-naphthylamine or elimination of NH_3 to naphthalene (cf. scheme 2).

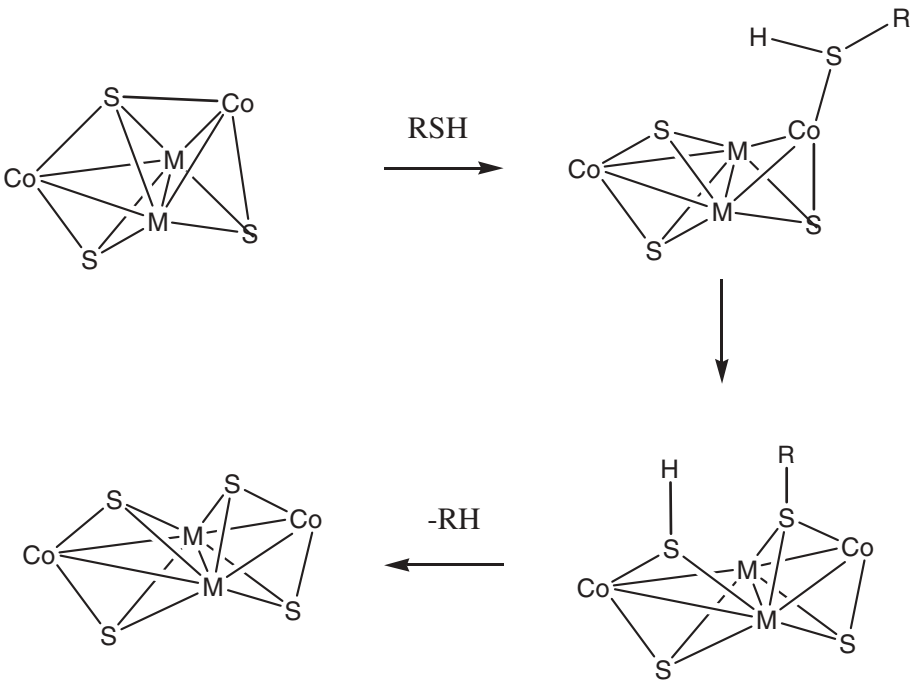
A final comment is appropriate about the small amount of 5,6,7,8-tetrahydro-1-naphthylamine observed in the HDN product of 1-naphthylamine. This product is due to hydrogenation of the non-substituted aromatic ring. Since the reactivity of 5,6,7,8-tetrahydro-1-naphthylamine itself is low, its low concentration in the HDN of 1-naphthylamine points to a slow rate of formation. This may be due to a weaker adsorption of the benzene part than that of the aniline part of the naphthylamine. The behavior of 1,2,3,4-tetrahydro-1-naphthylamine and 5,6,7,8-tetrahydro-1-naphthylamine in the HDN of 1-naphthylamine would then be similar to that of 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline respectively in the HDN of quinoline [9]. The small amount of 5,6,7,8-tetrahydro-1-naphthylamine produced and its low reactivity show that 5,6,7,8-tetrahydro-1-naphthylamine plays only a minor role in the HDN of 1-naphthylamine under our conditions.

4.2. Direct desulfurization

Aliphatic and aromatic thiols undergo HDS with high selectivity to alkanes and aromatic hydrocarbons, respectively. This suggests that in both cases hydrogenolysis of the C–S bond actually takes place. However, if amines do not react by real hydrogenolysis, then the question arises as to whether or not the direct C–S bond breaking in thiols takes place by real or apparent hydrogenolysis. An alternative explanation for the arylthiol would be partial hydrogenation followed by H_2S elimination (*e.g.*, thiophenol reacts to 1,2-dihydrothiophenol and then to benzene and H_2S), as suggested above for the reaction of arylamines to aromatic molecules. This is not possible, however, for alkane thiols. Alkanes are the main product of the HDS reaction of alkane thiols at lower temperatures; the only



Scheme 5. Reaction from 1-naphthylamine to 1-thionaphthol by hydrogenation to dihydro-1-naphthylamine, followed by a Bucherer-like NH_2–SH exchange and dehydrogenation of the resulting dihydro-1-thionaphthol.



Scheme 6. Reaction of alkyl- and arylthiols on homogeneous $Cp*_2Mo_2Co_2S_3(CO)_4$ clusters ($Cp* = C_5(CH_3)_5$) [3].

possible explanation is actual hydrogenolysis. Homolytic C–S bond scission (hydrogenolysis) was demonstrated by Curtis and Drucker in the homogeneous reaction of aliphatic and aromatic thiols with the $Cp*_2Mo_2Co_2S_3(CO)_4$ cluster (Cp* stands for pentamethylcyclopentadienyl) [3]. By spectroscopic and kinetic measurements, they showed that the thiols react as indicated in scheme 6, where only the bare structure of the complexes is indicated. The μ_3-mode of coordination of the RS thiolate leads to the activation of the C–S bond for homolytic cleavage by decreasing the C–S bond dissociation energy. The soft character of sulfur apparently enables a relatively strong interaction with the soft, low-valent Mo atoms in the metal sulfide; this promotes C–S bond homolysis, as observed in thiolate complexes [18]. The interaction of the nitrogen atom in an amine with such Mo atoms does not, on the other hand, lead to C–N bond scission because the μ_3-bonded, harder N atom is less strongly bonded as the equivalent S atom.

5. Conclusions

HDN of 1-naphthylamine over sulfided $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts leads to the formation of tetralin and naphthalene. The high selectivity to 1,2-dihydronaphthalene at low conversion of 1-naphthylamine shows that one of the HDN pathways is partial hydrogenation of 1-naphthylamine followed by NH_3 elimination. Naphthalene forms with high selectivity, even at low conversion. This apparent hydrogenolysis can be explained by hydrogenation of 1-naphthylamine to 1,2-dihydro-1-naphthylamine followed by NH_3 elimination. Another possible mechanism is hydrogenation of 1-naphthylamine to dihydro-1-naphthylamine, which undergoes a Bucherer-type NH_2–SH exchange, followed by dehydrogenation to 1-thionaphthol and hydrogenolysis to naphthalene.

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